

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)

09/980850

INTERNATIONAL APPLICATION NO.

PCT/US99/14393

INTERNATIONAL FILING DATE

25 JUNE 1999 (25.06.99)

PRIORITY DATE CLAIMED

25 JUNE 1999 (25.06.99)

TITLE OF INVENTION

COLORED POLYVINYL BUTYRAL INTERLAYER WITH IMPROVED HAZE PROPERTIES

APPLICANT(S) FOR DO/EO/US

PHILLIPS, Thomas Richard

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to bring national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b)) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application was filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau.
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☐ A translation of the International Application into English (35 U.S.C. 371 (c) (2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c) (3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included :

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A FIRST preliminary amendment.
A SECOND or SUBSEQUENT preliminary amendment.
16. ☐ A substitute specification.
17. ☒ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail.
19. ☐ Other items or information:

17. General Power of Attorney

18. Express Mailing Label No.: EJ376014396US

09/980850

PCT/US99/14393

AD-6621

0 OCT 2001

The following fees are submitted

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☒ Search Report has been prepared by the EPO or JPO \$890.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) \$710.00
- ☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$740.00
- ☐ Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,040.00
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) And all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00

CALCULATIONS PTO USE ONLY

ENTER APPROPRIATE BASIC FEE AMOUNT

=

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

☐ 20 ☒ 30

\$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total Claims	6 - 20 =	0 x	\$18.00
Independent Claims	1 - 3 =	0 x	\$80.00
Multiple Dependent Claims (check if applicable)			<input checked="" type="checkbox"/>

\$280.00

TOTAL OF ABOVE CALCULATIONS

=

\$280.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).

☐

\$0.00

SUBTOTAL

=

\$410.00

Processing Fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).

☐ 20 ☐ 30

\$0.00

TOTAL NATIONAL FEE

=

\$1,300.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐

\$0.00

TOTAL FEES ENCLOSED

=

\$1,300.00

Amount to be :
Refunded \$

Charged \$

☐ A check in the amount of _____ to cover the above fees enclosed.

☒ Please charge my Deposit Account No. **04-1928** in the amount of **\$1,300.00** to cover the above fees.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **04-1928** a duplicate copy of this sheet is enclosed.

NOTE : Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (CFR 1.37(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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DOBSON, KEVIN S.

NAME

40,296

REGISTRATION NUMBER

DATE

10/26/01

09/930650

TITLECOLORED POLYVINYL BUTYRAL INTERLAYER WITH IMPROVED HAZE PROPERTIES.

5

BACKGROUND OF THE INVENTION

The present invention relates to an improved process for preparation of colored thermoplastic composite sheeting for use in laminated structures. More particularly, the invention relates to laminated structures useful in automotive and architectural application that are colored or produced with a colored gradient band (GBT) for aesthetic and sun-blocking properties.

Commercially available GBT material produced prior to the mid- to late-1970's used dyes for coloring. Because dyes are virtually completely soluble in a polyvinyl butyral (PVB) matrix, they produced very aesthetic looking products. However, even when used with light stabilizers, dyes are subject to fading due to ultraviolet radiation.

Weathering is particularly a problem in architectural applications where product life times of twenty years might be required. For this reason, many of the commercially available products have switched from dyes to organic and inorganic pigments for coloring. Various approaches for using the pigments have been tried; however, problems of agglomeration of the pigment containing medium, limited shelf life due to dissimilarity of viscosities of the medium and the polymer, dispersion of the solvent in the medium into the polymer with reduction of adhesion between the PVB sheet and glass as well as undesirable haze have been experienced.

It is therefore an object of this invention to provide colored and gradient band PVB interlayers that are free from the problems previously experienced.

Numerous patents disclose the use of pigments as uniform or band colorants for PVB. USP 4,316,868 (issued to Monsanto, nee Solutia) states (col. 5, line 10) "The polymer extruded through the probe can be dyed or pigmented to produce the desired color. The pigment should be adequately dispersed at all times to give best results."

Japanese Patent Application 2-272068 (Mitsubishi Monsanto) claims the use of a plasticizer-based ink wherein the pigment concentration is 20 percent maximum (with the use of dispersants), the average particle size is less than 2.5 micrometers and the pH is controlled to between 4 and 10.

- 5 Japanese Patent Application JP 9-183638 (Sumika Color KK) claims an apparent chip material made from a rosin-modified maleic acid resin. In this application the chip type material must be first dissolved in plasticizer then undergo additional bead milling before combining with PVB to make sheeting.

- 10 Japanese Patent Application 2-272068 purports to overcome manufacturing and product problems associated with using ink injection into an extruder in making uniformly colored PVB. Pigment aggregation, an aesthetic, visual problem is overcome by controlling the pigment particle size and pH and using a dispersant in the ink composition.

- 15 Japanese Patent Application 9-183638 also provides a plasticizer-based dispersion but by pre-processing the colorant in a rosin-modified maleic acid binder resin. This chip type system is partially soluble in plasticizer, must undergo additional bead milling and is only blended with the PVB before pressing sheeting material. However, because of its acid functionality, it would be expected that under extrusion processing conditions, such a binder resin
20 would readily cross-link with the PVB resin and result in processing difficulties, i.e., uncontrollable viscosity changes.

- Further, in coating type applications as describe later, such a binder resin would have little affinity for glass and, therefore, would be non-functional in providing a laminated safety product.

25

SUMMARY OF THE INVENTION

- A laminar structure comprised of at least two layers of glass and a sheet of plasticized PVB is prepared by providing a color concentrate comprised of solid pigmented chips wherein the chips have a preselected pigment particle size range
30 to minimize haze in the laminated structure and are dispersed in a low molecular weight polyvinyl butyral resin, said chips comprising from about 10 to 60 weight percent of the color concentrate, depositing said color concentrate on a roughened

surface of polyvinyl butyral sheeting as a dried colored coating or directly melt incorporating, and thereafter laminating said sheeting between the surfaces of layers of glass.

By "preselected pigment particle size it is meant a mean pigment particle size from about 50 to 500 nanometers.

Because of the particulate nature of pigments, it is critical that the particle size of the pigments be as small as possible to maintain the high transparency and low haze that is the norm for dye-based colored products. In accordance with this invention it has been found that direct use of chip concentrates – typically roll-milled pigment/binder solid concentrates, where the binder is a low molecular weight PVB resin, give colored laminates having excellent haze characteristics.

It has now been found that when used to color PVB either as a solid colorant or as a letdown ink, chips provide a higher quality product in terms of transparency and haze, as well as a less complex route for adding the concentrate.

The chips, based on commercially available low molecular weight PVB's, do not result in gelation or cross-linking of the PVB, a problem often encountered with high molecular weight or functionalized binder resins. Further, the low molecular weight binders do not interfere in any way with the performance of the final laminated product.

Further, the resulting ground chip product can be used directly in extrusion operations or can be made into inks with suitable solvents for printing applications.

DETAILED DESCRIPTION OF THE INVENTION

Plasticized polyvinyl butyral (PVB) resin is the preferred polymer for making laminated safety glass constructions used in the automotive and architectural industries. Plasticized PVB sheeting is prepared by well known processes. Preparation of plasticized PVB is disclosed in Phillips, U.S. 4,276,351 that is hereby incorporated by reference. It is common practice in both applications to uniformly color the PVB or to add a colored gradient band on the plasticized PVB sheeting by processes well known in the art.

It has been found that the use of pigmented chip color concentrates based on low-molecular weight PVB resins provides a method of achieving lower haze in both uniformly colored PVB and gradient band PVB than is currently commercial available with pigmented products produced by other methods.

5 Further, these chips may be used directly in all known PVB processes without additional processing.

Chips are typically prepared in a heated two-roll mill process where the combined pigment, a compatible binder resin for the end-use application and, sometimes, dispersing agent(s) are subjected to high shear near the melting point of the binder resin. The resulting slabs are broken up into workable size particles called chips.

The particle size of the pigments prepared according to the above process from commercially available pigments is nominally an order of magnitude smaller than those described in the referenced Japanese Patent Application 2-272068 and equal to or slightly larger than those disclosed in Japanese Patent Application 9-183638.

The chips can be used directly in extrusion operations to make either uniformly colored PVB or co-extruded gradient band PVB. Because of the smaller pigment particle size, chips do not form aggregations when used directly in extrusion processes. Further, because chips are solids and can be added directly with the polymer feed to the extruder, it is not necessary to develop injection capabilities as those described in US Patent 3,679,788 or dissolve them in plasticizer as described in Japanese Patent Application 9-183638.

Further, solids are far easier to handle than liquids, thereby eliminating spill and contamination concerns and the like.

However, while not soluble in plasticizer, if desirable, the chips according to the present invention could be ground to a very small size, be dispersed in plasticizer and fed to extrusion processes previously described.

Chips can also be letdown to make printing inks using appropriate solvents or can be mixed with end-use resin to either be used directly as feed or extrude to produce letdown pellets for subsequent direct use.

The following examples in which parts and percentages are by weight unless otherwise indicated further illustrate the invention.

EXAMPLE 1

5 Black, blue and red pigmented color chips were commercial prepared by Penn Color Inc. according to specifications which follow. The chip contained nominally 40 percent of a commercially available pigment and 60 percent Mowital® B30T, a commercially available PVB resin. Mowital® B30 series resins have a solution viscosity of 20-30 centipoise and Mowital ® B60 series
10 resins a solution viscosity 60-90 centipoise. (The solution viscosity that is a measure of molecular weight was determined using Brookfield solution viscosity data for the resins measured at 20 degrees C as a 5% solution in n-butanol.) Both performed acceptably in the preparation of the chip formulations. PVB resin typically used to produce sheeting having a solution viscosity of 130-140 did not
15 perform acceptably. Particle size analysis indicated the mean size of the pigments to be between 100-300 nanometers.

A dark blue ink batch was prepared by letting the chips down along with additional PVB resin for viscosity control and 3:1 methanol:toluene solvent.

20 The ink was coated and transferred to PVB sheeting according to procedures described in US Patents 5,487,939 and 5,607,726.

The gradient band sample was laminated between glass sheets according to normal lamination techniques. The sample was transparent, did not exhibit pigment agglomeration or diffuse light when back-lighted by a high intensity
light.

COMPARATIVE EXAMPLE A

25 A composite blue ink was prepared according to conventional media-mill techniques using a Dyno mill with zirconia media. Black, blue and red pigments were combined with PVB resin for viscosity control and 3:1 methanol:toluene solvent and milled for nominally 48 hours at which time it was filtered through
30 nominally 3 micron filters.

The ink was coated, transferred to PVB sheeting and laminated as in Example 1. The sample was transparent, did not exhibit pigment agglomeration but did diffuse light when back-lighted by a high intensity light.

The laminates prepared in Example 1, Comparative Example A and a commercially available laminate containing pigmented gradient band Saflex®, (Solutia's nee Monsanto's trademark for its PVB sheeting) PVB were measured for haze using a Hunter Laboratories UltraScan® II Sphere Spectrocolorimeter.

The results in Table 1 show that the laminate prepared according to Example 1 has lower haze than either the comparative example or the commercially available product. The lower haze is attributed to smaller pigment particle size and narrower distribution verses the media-mill colorant and to lack of pigment agglomeration verses the commercially available co-extruded product.

Table 1

<u>Sample</u>	<u>Colorant Process</u>	<u>Diffuse % Transmission</u>	<u>Total % Transmission</u>	<u>Haze</u>
Example 1	Chip	0.11	39.78	0.29
Comparative Example A	Media-Mill	1.94	42.7	4.55
Saflex®	Unknown	0.23	40.41	0.58

EXAMPLE 2

The chips used for Example 1 were dry fed to an extrusion process making uniformly colored gray PVB sheeting. The sheeting was laminated as described in Example 1. The laminate of Example 2 and a laminate of commercially available uniformly colored gray pigmented Saflex® PVB were measured for haze as previous described.

The results in Table 2 show that Example 2 has lower haze than the commercially available product.

Table 2

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<u>Sample</u>	<u>Colorant Process</u>	<u>Diffuse %</u> <u>Transmission</u>	<u>Total %</u> <u>Transmission</u>	<u>Haze</u>
Example 2	Chip	0.07	44.05	0.16
Saflex®	Unknown	0.26	42.68	0.62

CLAIMS:

1. A process for preparing colored thermoplastic composite sheeting for use in laminated structures comprising providing a color concentrate comprised of solid pigmented chips wherein the chips have a preselected pigment particle size range to minimize haze in the laminated structure and are dispersed in a low molecular weight polyvinyl butyral resin, said chips comprising from about 10 to 60 weight percent of the color concentrate, depositing said color concentrate on a roughened surface of polyvinyl butyral sheeting as a dried colored coating or directly melt incorporating, and thereafter laminating said sheeting between the surfaces of two layers of glass.
2. The process of claim 1 wherein said solid pigmented chips have a mean pigment particle size from about 50 to 500 nanometers.
3. The process of claim 1 wherein the low molecular weight polyvinyl butyral has a Brookfield solution viscosity from 20-90 centipoises when measured at 20°C as a 5% solution in n-butanol.
4. A glass laminate prepared in accordance with claims 1, 2, or 3.

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

COLORED POLYVINYL BUTYRAL INTERLAYER WITH IMPROVED HAZE PROPERTIES

the specification of which is attached hereto unless the following box is checked:

☒ was filed on **25 JUNE 1999** as U.S. Application No. _____ or PCT International Application No.

PCT/US99/14393 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
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I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.

U.S. Provisional Application No.

U.S. Filing Date

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)
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POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Name: **KEVIN S. DOBSON**

Registration No.: **40,296**

Send correspondence and direct telephone calls to:

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(302) 992-2953

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

INVENTOR(S)

Full Name of Inventor	Last Name PHILLIPS	First Name THOMAS	Middle Name RICHARD
	Signature (please sign full name): <i>Thomas Richard Phillips</i>		Date: 11/09/01
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			Zip Code 26105

☐ Additional Inventors are being named on separately numbered sheets attached hereto.